

# PATENT SPECIFICATION

(11) 1 269 096

1 269 096

## NO DRAWINGS

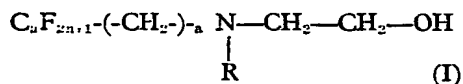
- (21) Application No. 41720/69 (22) Filed 21 Aug. 1969  
 (31) Convention Application No. 163 588 (32) Filed 21 Aug. 1968 in  
 (33) France (FR)  
 (45) Complete Specification published 29 March 1972  
 (51) International Classification C 07 c 91/06  
 (52) Index at acceptance  
 C2C 20Y 31I 31Y 322 323 32Y 360 361 36Y 456 45Y  
 502 50Y 620 623 633 730 733 796 797 LD



## (54) METHOD FOR THE PREPARATION OF POLYFLUORINATED AMINOALCOHOLS

(71) We, UGINE KUHLMANN, a French Body Corporate, of 10, Rue du General Foy, Paris 8e, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

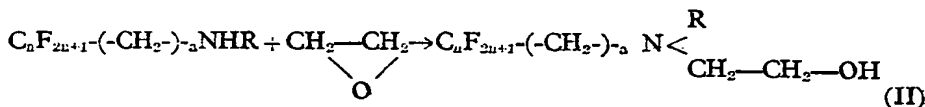
This invention relates to a method for the preparation of polyfluorinated aminoalcohols of general formula:



wherein:

$\text{C}_n\text{F}_{2n+1}$  represents a straight or branched perfluorinated alkyl chain,  $n$  being an integer between 1 and 20 both inclusive, preferably between 6 and 12 both inclusive,  $a$  is 2 or 4, and R represents a hydrogen atom or the radical  $-\text{CH}_2-\text{CH}_2-\text{OH}$ . Such compounds are claimed *per se* in Applicant's United Kingdom Letters Patent No. 1218759.

According to the present invention a method for the preparation of polyfluorinated aminoalcohols comprises reacting ethylene oxide with a polyfluorinated amine or aminoalcohol according to the reaction scheme:

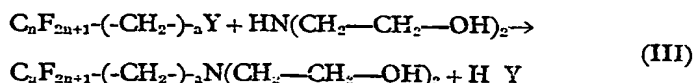


wherein:

$n$ ,  $a$ , R are as defined above.

United Kingdom Patent Specifications Nos. 1,210,842 and 1,218,759, and the respective Patents of Addition Applications thereto Nos. 21840 and 21841/69 (Serial Nos. 1269094

and 1268939) describe a method for the preparation of these polyfluorinated amines and aminoalcohols respectively. In the methods described therein, diethanolamine is reacted with a polyfluoroalkane halide according to the reaction:



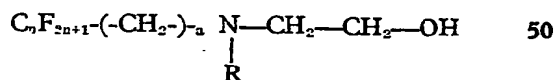
(wherein Y = I or Br)

This method is preferred when  $a$  is equal to 4, but gives poor results when  $a$  is equal to 2, forming a large quantity of polyfluorinated olefine  $\text{C}_n\text{F}_{2n+1}-\text{CH}=\text{CH}_2$ .

For the present invention it is preferred to use aminoalcohols as starting material, i.e. when R is  $-\text{CH}_2-\text{CH}_2-\text{OH}$ .

According to the present invention a method [Price 25p]

for the production of polyfluorinated aminoalcohols of general formula:

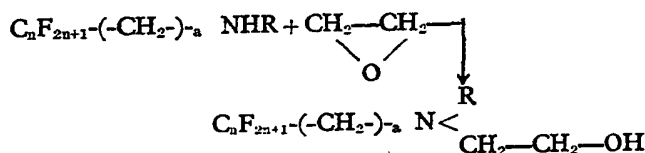


wherein:

$\text{C}_n\text{F}_{2n+1}$  represents a straight or branched

perfluorinated alkyl chain,  $n$  being an integer between 1 and 20 both inclusive,  $a$  is 2 or 4, and  $R$  represents a hydrogen atom or the radical  $-\text{CH}_2-\text{CH}_2-\text{OH}$ , comprising react-

ing ethylene oxide with a polyfluorinated amine or amino alcohol according to the reaction:



The polyfluorinated amine or aminoalcohol may be present alone or dissolved in a solvent inert towards the polyfluorinated compound and the ethyl oxide. The preferred solvents are ether, for example di-ethyl ether or dioxan, a ketone, for example acetone, aliphatic or aromatic hydrocarbons, for example benzene and toluene. The reaction temperature is suitably between  $15^\circ\text{C}$  and  $140^\circ\text{C}$ , preferably between  $30^\circ\text{C}$  and  $100^\circ\text{C}$ . Dependant on the chosen reaction temperature, the reaction may be carried out in an autoclave under autogenous pressure.

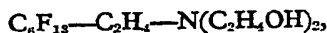
The polyfluorinated aminoalcohols have many uses, in particular, in the textile industry and in the leather, paper, and plastics com-

pounds industries. Added to plastics compounds, they give them plastifying and auto-lubricating properties and improve their surface properties. Thanks to their chemical stability and their surface properties, these products find their applications as tensio-active agents in mediums such as water, organic solvents, diluted or concentrated acids, and diluted or concentrated alkalis. They may also be used as levelling agents which, because of their surface properties, facilitate the spreading of viscous products, such as waxes, greases, varnishes and paints over large areas. Examples of the various properties of the polyfluorinated aminodiols can be seen in Table 1:

TABLE 1

Decrease in the Surface Tension	$\text{C}_n\text{F}_{2n+1}-\text{C}_2\text{H}_4-\text{N}(\text{C}_2\text{H}_4\text{OH})_2$		
	$\text{C}_n\text{F}_{2n+1} = \text{C}_6\text{F}_{13}$	$\text{C}_n\text{F}_{2n+1} = \text{C}_8\text{F}_{17}$	$\text{C}_n\text{F}_{2n+1} = \text{C}_{10}\text{F}_{21}$
of water (dyne/cm)	18.1 (1000 ppm)	15.8 (100 ppm)	20.5 (10 ppm)
	17.9 (200 ppm)	15.8 (10 ppm)	25°C
	25.0 (50 ppm)		
	36.2 (25 ppm)	25°C	
of sulphuric acid at 80% (dyne/cm)	32.2 (100 ppm) at $20^\circ\text{C}$	17.8 (100 ppm) 25°C	
of NaOH in aqueous solution at 15% by weight (dyne/cm)	31.9 (10 ppm) at $20^\circ\text{C}$		

The damping power of



dissolved at the rate of 1000 ppm in water, is 53 seconds. The damping power is taken as the falling time of a tissue disc in an aqueous

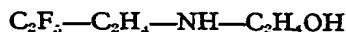
solution of the product at  $20^\circ\text{C}$ . The foaming power of the same product for the same concentration is 400, 380 and 370—these values being measured after 30 seconds, 3 minutes and 5 minutes. Foaming power is determined according to the ISOTC 91—182F standard test by measuring the volume of foam obtained

after 500 ml of an aqueous solution of the agent to be tested, maintained at 20°C, is poured onto a surface of the same solution.

- 5 The invention will now be further described with reference to the following Examples in which when a fraction contains several constituents, the percentages are given as molar percentages of the various compounds and the yields are referred to the starting fluorinated material.

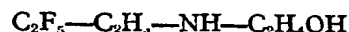
#### EXAMPLE 1

Ethylene oxide (20 g; 0.45 mole) was bubbled for 3 hrs through

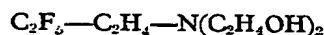


- 15 (29 g; 0.14 mole) under constant stirring. During the addition of the ethylene oxide the temperature rose from 24°C to 36°C. The reaction medium was then distilled and two fractions obtained:

- 20 *a*-fraction 85°C/10 mm; 7 g; consisting of:

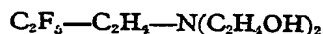


(97%; 32.5 mole) and

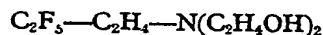


(3%; 1.1 mmole).

- 25 *b*-fraction 115°C/2mm; 22.4 g; consisting of:



(89 mmole)



- 30 had been obtained with a conversion rate of 63.5% and a yield of 83%.

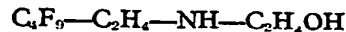
#### EXAMPLE 2

Ethylene oxide (20 g; 0.45 mole) was bubbled for 3 hrs through

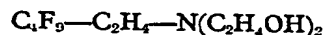


- 35 (28 g; 0.091 mole) under constant stirring. During the addition of ethylene oxide the temperature rose from 25°C to 38°C. The reaction medium was then distilled and two fractions obtained:

- 40 *a* fraction 105°C/10 mm; 5.3 g; consisting of



(96%; 16.5 mmole) and

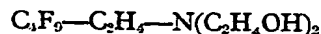


(4%; 0.7 mmole).

- b* fraction 126°C/2 mm; 23 g; consisting of 45



(65.5 mmole)

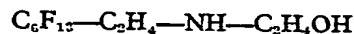


had been obtained with a conversion rate of 73% and a yield of 89%.

50

#### EXAMPLE 3

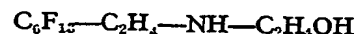
Ethylene oxide (89 g; 2 mole) was passed through a fritted glass into



(550 g; 1.27 mole) maintained to 60°C which was constantly stirred. The reaction medium was then distilled and three fractions and one residue obtained:

55

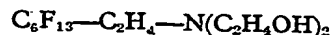
- a* fraction <128°C/1 mm; 15 g; consisting of



60

and two unidentified compounds

- b* fraction 128°C/0.7 mm; 517 g; consisting of



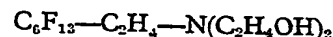
(1.15 mole)

- c* fraction 128°C—140°C/0.7 mm; 10 g; consisting of 65



and two unidentified compounds

- d* residue 20 g. This residue consisted mainly of polymers of ethylene oxide. 70



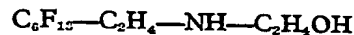
had been obtained with a conversion rate of 90.5%.

#### EXAMPLE 4

Ethylene oxide (27.3 g; 0.62 mole) was bubbled for 3 hrs at 30°C through a mixture of  $\text{C}_6\text{F}_{13}-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4\text{OH}$  (81.4 g; 0.2 mole) and ethyl ether (150 cm<sup>3</sup>) under constant stirring. The reaction medium was then distilled and the ethyl ether solvent and two other fractions obtained:

80

- a* fraction 116°C/8 mm; 47.8 g; consisting of



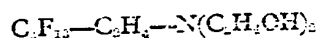
(96%; 111 mole) and



(4%; 5.7 mmole)

85

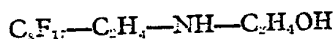
b fraction 130°C/0.8 mm; 30.1 g; consisting of  $C_6F_{13}-C_2H_4-N(C_2H_4OH)_2$  (66.5 mmole)



5 had been obtained with a conversion rate of 36% and a yield of 31%.

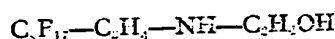
#### EXAMPLE 5

Ethylene oxide (44 g; 1 mole) was bubbled for 6 hrs at 60°C through



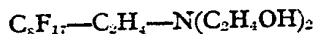
10 (200 g; 0.394 mole). The reaction medium was then distilled and two fractions obtained. During the distillation, the condenser placed at the head of the column was fed with water maintained at a temperature of from 50°C to 60°C because the reaction product is solid at ambient temperature.

a fraction <140°C/1 mm; 7 g; consisting of two unidentified compounds and

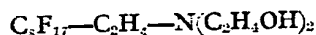


20 (87%)

b fraction 140°C/0.5 mm; 186.6 g; consisting of



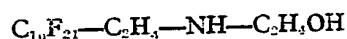
25 having a degree of purity of 99% (0.339 mole) melting at 42°C



had been obtained with a conversion rate of 86%.

#### EXAMPLE 6

30 Ethylene oxide (20 g; 0.45 mole) was bubbled for 1 hr at 90°C through

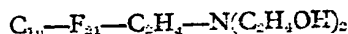


35 (108 g; 0.178 mole). The reaction medium was then distilled and two fractions and a residue obtained. During the distillation, the condenser placed at the head of the column was fed with water maintained at a temperature from 80°C to 90°C because the reaction product is solid at ambient temperature.

40 a fraction <140°C/0.2 mm; 7 g; consisting of

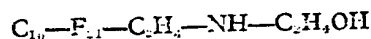


(94.8%; 11 mmole) and

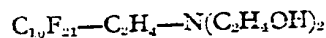


(5.2%; 0.6 mmole)

b fraction 160°C-170°C/0.2 mm; 91.3 g; consisting of

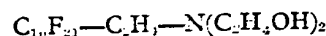


(4.7%; 6.6 mmole) and



(95.3%; 134 mmole)

c residue 4.7 g unidentified solid



had been obtained with a conversion rate of 75% and a yield of 83%.

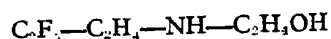
#### EXAMPLE 7

Ethylene oxide (21 g; 0.475 mole) was bubbled for 2 hrs at 25°C through



(22.5 g; 0.138 mole). During the addition of the ethylene oxide the temperature rose from 25°C to 40°C in 15 minutes and then fell gradually to the initial temperature. The reaction medium was then distilled and two fractions obtained:

a fraction 85°C/10 mm; 4.3 g; consisting of

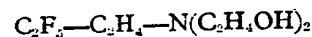


(98%; 23 mmole) and two unidentified compounds

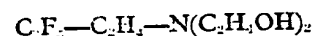
b fraction 115°C/2mm; 19.6 g; consisting of



(2%; 2 mmole) and



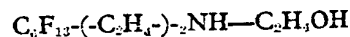
(98%; 76.5 mmole)



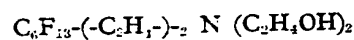
had been obtained with a conversion rate of 55.5%.

#### EXAMPLE 8

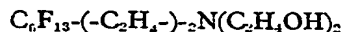
Ethylene oxide (25 g; 0.57 mole) was bubbled for 2 hrs through



(44 g; 0.101 mole). During the addition of the ethylene oxide the temperature rose from 20°C to 30°C in 20 minutes and remained at 30°C for 1 hour. 47 g of a viscous liquid consisting of 95% of



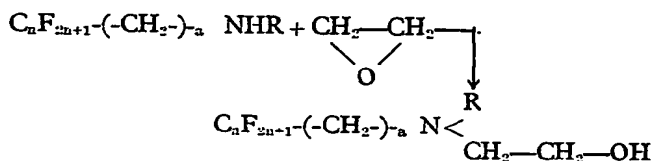
were collected. The boiling point of this polyfluorinated aminodiols was between 135°C and 140°C under 0.8 mm pressure.



- 5 had been obtained with a conversion rate of 92%.

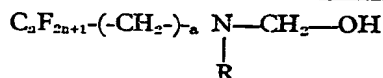
WHAT WE CLAIM IS:—

1. A method for the production of polyfluorinated aminoalcohols of general formula:



20

2. A method according to Claim 1, wherein  $n$  is an integer between 6 and 12 both inclusive.  
 3. A method according to Claim 1 or Claim 2, wherein the reaction is carried out at an operative temperature of from 15°C to 140°C.  
 25 4. A method according to Claim 3, wherein the operative temperature is between 30°C and 100°C.  
 5. A method according to any of Claims 1 to 4, wherein the reaction carried out in the presence of a solvent which is inert towards the reactants and the final product.  
 30 6. A method according to Claim 5, wherein the solvent is an ether, a ketone, an aliphatic hydrocarbon or an aromatic hydrocarbon.  
 35 7. A method according to Claim 6, wherein the ether is di-ethyl ether or dioxan.  
 8. A method according to Claim 6, wherein the ketone is acetone.



10

wherein:

$C_nF_{2n+1}$  represents a straight or branched perfluorinated alkyl chain,  $n$  being an integer between 1 and 20 both inclusive,  $\alpha$  is 2 or 4, and  $R$  represents a hydrogen atom or the radical  $-CH_2-CH_2-OH$ , comprising reacting ethylene oxide with a polyfluorinated amine or aminoalcohol according to the reaction:

15

9. A method according to Claim 6, wherein the aromatic hydrocarbon is benzene or toluene.

40

10. A method according to Claim 1, substantially as herein described.

11. A method for the production of polyfluorinated aminoalcohols as herein described with reference to any of Examples 1 to 8.

45

12. Polyfluorinated aminoalcohols whenever prepared by the method of any of Claims 1 to 11.

50

PAGE, WHITE & FARRER,  
 Chartered Patent Agents,  
 27, Chancery Lane,  
 London, W.C.2.  
 Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.  
 Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

**THIS PAGE BLANK (Usr 1.1)**